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^{13}C and ^{15}N Solid State NMR of Copolymers of Nylons 6 and 7: Observation of a Stable Pseudohexagonal Phase

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ABSTRACT

We have synthesized and characterized a series of nylon copolymers based on the even-odd A-B monomer combination, caprolactam and enantholactam. The nylon 6-co-7 samples obtained were found to possess physical properties which directly correlate with copolymer composition. We have determined degrees and types of crystallinity for these materials using a combination of thermal, NMR and X-ray measurements. The homopolymers each display highly ordered α-crystallites while the copolymers possess less-ordered domains that decrease in α-like characteristics down to the 1:1 copolymer which possesses a thermodynamically stable pseudohexagonal ordered phase. The ^{13}C T_1 values determined for the annealed 1:1 copolymer were shorter than those of crystalline regions of homopolymers, comparable to those observed for amorphous domains in melt quenched nylon 6 and nylon 7 homopolymers, and significantly longer than the values for precipitated and annealed 1:1 nylon 11-co-12 sample. Annealing at temperatures ca 10 °C below the DSC T_m increased the perfection of the copolymer ordered domains based on both NMR and X-ray measurements, but did not convert the pseudohexagonal phase to α-crystallites.

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INTRODUCTION AND BACKGROUND

Piezoelectric materials possess the unique ability to interconvert mechanical and electrical energy.[1] Applications involve, on the one hand, the conversion of a pressure or sound wave into an electrical signal that can be processed and analyzed, and on the other the transformation of a voltage change into mechanical motion. The piezoelectric properties of odd A-B nylons (eg., nylon 7 and nylon 11) have been under study for only a few years.[2] The relationship between molecular and microscopic order and the macroscopic behavior of the odd nylons is only now beginning to become clear. Especially important are recent results indicating <u>increased</u> piezoelectricity with increasing temperature, even up to the melt.[3] This can be compared to a large reduction in electrical properties for poly(vinylidene fluoride) when heated much above it's T_g. Early work on the crystal forms and transformations of nylon 11 illustrates the lack of molecular level understanding: for years it was thought that the α-δ (or Brill) transition[4] that occurs at 95°C involved rapid amide group rotation around the chain axis involving 60° jumps.[5] We have used solid state NMR methods to confirm that such reorientation does not occur in the nylon 11 crystalline domains between the Brill transition and the melting point.

Solid state nuclear magnetic resonance (NMR) has been shown to be a unique spectroscopic tool for determining molecular composition, crystallinity, packing, orientation and motion in as-obtained and end-use materials. We have applied several NMR methods to evaluation of the molecular-level properties and behavior of nylons. Observation of different nuclei (^{13}C and ^{15}N) allows determination of segmental properties within crystalline domains, amorphous regions and the interphase between the two. We

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A-1

used variable temperature solid state NMR techniques, including ^{13}C and ^{15}N cross polarization/magic angle spinning (CP/MAS) and high power decoupling/magic angle spinning (HP/MAS) observation[6] along with wide-line ^{2}H analysis of ^{2}H-N labeled samples,[7] to prove that rapid amide bond reorganization did not occur in the nylon 11 δ-phase. These results confirmed that the rigid hydrogen-bonded network that exists in the crystalline domains of nylons is maintained even at temperatures close to the crystalline melting point, a conclusion consistent with the high temperature piezoelectric behavior recently reported.[3]

Random nylon copolymers of A-B monomers are just beginning to be intensively investigated. Ring-opening copolymerizations of lactams have been rarely studied despite the fact that high molecular weight homopolymers are obtained rapidly and efficiently. Studies of A-B copolymers include ring-opening polymerization of caprolactam (nylon 6 monomer) with laurolactam (nylon 12) to give nylon 6-co-12 samples,[8] and reaction of the lactam for nylon 8 with laurolactam to give the corresponding nylon 8-co-12 polymers.[9] The condensation polymerization of activated amino esters to give odd terpolyamides has also been reported.[10] We have recently described initial results with nylon 11-co-12 polymers obtained by thermal polycondensation of the corresponding amino acids.[11] The present report describes the copolymerization of caprolactam with enantholactam to give nylon 6-co-7 samples. Our interest in these materials concerns the role disruption of the polar piezoelectric α-nylon 7 crystallites by the nylon 6 units might have an processability and electrical properties (Figure 1).

Experimental

Anionic ring-opening polymerization of lactams by themselves and in various mixtures was initiated with NaH using N-acetylcaprolactam as co-initiator. Polymerizations were carried out in small test tubes under N_2 atmosphere with rapid conversion at temperatures ranging from 80-150 °C. Small amounts of residual lactam monomers (observed in all cases) were removed by reprecipitation or methanol extraction. For comparison purposes, mixtures of the appropriate 6- and 7-carbon amino acids were subjected to thermal polycondensation under nitrogen purge to give nylon 6-co-7 copolymers of similar compositions.

Characterization involved viscosity, differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7, solution NMR (^{1}H and ^{13}C) using 3:2 mixtures of trifluoroethanol (TFE) with CH_2Cl_2 on a Bruker AC-300 spectrometer, and solid state ^{13}C and ^{15}N NMR on Bruker MSL-200 and MSL-400 spectrometers using conditions described previously referenced respectively to the adamantane methine peak at 29.5 ppm and the glycine peak at 0 ppm.[6,11]

Results and Discussion

Ring opening polymerizations of these two lactams to give copolymers was fast, clean and occurred in high yields. Removal of residual monomer by extraction or precipitation from TFE-CH_2Cl_2 mixtures into acetone gave pure polymers. Viscosities were obtained in this same solvent mixture and films could be cast if appropriate care was taken to eliminate water and allow slow solvent evaporation during the casting process. Inherent viscosities ranged from 2-4 dL/g (at 0.5 g/dL) confirming formation of

high molecular weight polymers. This solvent system is an excellent one for high resolution NMR in that it gives relatively low viscosity, high concentration solutions.[12]

Solution NMR characterization of the copolymers was used to confirm overall compositions. Figure 2 gives representative ^{13}C spectra illustrating separation of peaks for the two repeat units which allows approximate determination of repeat unit ratios. No indication is apparent of additional sequence information such as diad or triad peaks. Good correlation of composition (based on peak heights) to feed ratio was observed, although there appeared to be a slightly higher incorporation of the nylon 7 monomer unit in all copolymers studied. This is surprising given the high conversions used since even if preferential incorporation of one of the monomers was occurring early in the reaction, the drift in monomer ratio would lead to higher incorporation of the less reactive species near the end of the reaction. In fact, the 8-membered ring lactam has been reported to possess a higher reactivity compared to the 7-membered homolog, a difference which has been discussed in terms of enthalpy and entropy considerations.[13] In any event, based on the high heats of polymerization (allowing transamidation) and the fact that amino acid condensation polymers gave very similar compositions and identical properties to those of the lactam polymers, we believe random copolymerization occurred and the qualitative and quantitative observations made below reflect general correlations with composition.

Figure 3 gives the values determined by DSC for apparent melting points (T_m) and heats of fusion (ΔH_f) for the series of copolymers and the homopolymers synthesized under the same conditions. Excellent correlation is seen with composition similar to what was reported previously for nylon 8-co-12 and nylon 11-co-12 polymers. That is, gradual

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decrease in T_m and ΔH_f values to a minimum at ca 1:1 composition was observed. This is consistent with the idea of disruption of crystal packing and crystallinity due to mismatch of the number of CH_2 units in the two repeat unit structures within the overall hydrogen-bonded framework. In fact, it should be noted that the copolymers ranging from 30:70 to 70:30 compositions could all be solvent cast into transparent, colorless films. This indicates a low degree of crystallinity and/or very small crystallites as would be expected for mostly amorphous materials. However, DSC analysis did not reveal any significant glass transitions, and the lack of readily observable T_g's is inconsistent with highly amorphous samples. In addition, the strong melting points and enthalpies measured by DSC argue for ordered domain formation. NMR and X-ray data given below indicates that the copolymers do, in fact, form ordered arrays which do not possess the same type of crystallinity existing in the α- and γ-forms common to most nylons.

Solid-state NMR analysis of these samples clearly allows identification of the type and relative content of the normal crystal forms seen in nylons versus amorphous region. Figure 4 gives the ^{15}N spectra of precipitated, dried and then annealed samples. The sample history has a large effect on the type and degree of crystallinity. For example, annealing of the pure nylon 7 homopolymer greatly increased the relative height and sharpness of the α-form crystal peak (at 84 ppm). The precipitated nylon 6 sample showed peaks for both α- and γ-crystals (84 and 89 ppm, respectively), and annealing greatly increased the former at the expense of the latter. The intense α peaks for the homopolymers are consistent with previous reports of crystalline contents of 30-40 percent for annealed samples of these polymers.[13] It should be noted that nylon 7 adopts

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the α-crystal form[14] preferred for odd A-B nylons as seen for higher members of the homologous series including nylon 11.[15] Nylon 6 adopts the α-form in contrast to higher even-numbered polyamides, such as nylons 8, 10, and 12, which prefer the γ-form thermodynamically.[16] Nylon 6 is therefore at the borderline between higher members of the homologous series (γ-form preferred) and the lower members (nylons 2-5) all of which prefer the α-form.

The intermediate compositions show decreasing α-form peak with an increase in the broad peak located at ca 87 ppm. A broad peak at this position has been observed for the amorphous regions of all nylons examined by us to date by solid state ^{15}N NMR. Sharp peaks at this same chemical shift have been observed for the δ-form of nylon 11 (generated from the α-crystallites at temperatures above 95 °C) and for a meta-stable form of nylon 11 obtained by melt quenching. Both forms of nylon 11 generate X-ray patterns consistent with pseudohexagonal packing of chain segments.[17,18] This pseudohexagonal form is believed to possess arrays of chains ordered with respect to each other along the chain axis, but with no all-trans arrangement of the methylene segments and with random directional distribution of the amide groups down the chain. That is, while the backbones possess a more-or-less linear arrangement of segments down their axes, the hydrogen bonds between chains can exist with any (and all) of the six close-packed chains in the hexagonal array around it. The hydrogen bonds are thus arranged at 60° angles with respect to each other but with no sequential order. The 87 ppm peak for the copolymers thus appears to correspond to a combination of flexible amorphous domains and rigid pseudohexagonal regions.

The ^{15}N solid state NMR observations were based on results obtained using CP/MAS which does not discriminate among crystalline, amorphous or intermediate regions. The spectra are a thus composite (although not a quantitative one) of all domains present in the sample but with apparent emphasis on the crystalline peaks which are sharper and therefore more easily seen over the broader amorphous peak. With ^{13}C NMR analysis, higher natural abundance and better NMR response of ^{13}C over ^{15}N allows selective observation of the more rigid (ordered) domains with pulse programs such as that used for evaluation of T_1 relaxation times (CPT1 method).[19] The spectra in Figure 5 are of annealed samples obtained with the CPT1 pulse train although they are similar to spectra obtained with the normal CP/MAS method. The α-crystal forms of the two homopolymers give the C_N peak at 43.4 ppm, but there are clear differences for the tallest peak (at 30.1 ppm for nylon 6 and 31.6 ppm for nylon 7) and for the C_β peak (β to the carbonyl carbon) at 26.3 and 27.9 ppm, respectively. The ordered domain peaks for the copolymers are not averages of these but instead show a combination of two peaks that are roughly equivalent in relative intensities to the repeat unit contents in the copolymers. For example, the C_β peak for nylon 6 units decreases while a peak for the nylon 7 units increases with increasing nylon 7 content. Similarly, two peaks are seen in the intermediate compositions at ca 30 and 31.5 ppm for the most intense CH_2 peaks of the nylon 6 and 7 repeat units, respectively. In contrast is the C_N peak for the 1:1 copolymer (and to a lesser extent, the 35:65 and 65:35 samples), which should stay at the same chemical shift for the whole series but instead shows a slight up-field movement consistent with contributions to the peak from additional conformations approaching the

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non-planar or 60° twisted form of γ-crystallites of nylons. This indicates that the intermediate copolymers possess relatively ordered domains (since CPT1 observation was effective) with conformations around the amide groups ranging from α- to γ-like, exactly as expected for pseudohexagonal packing as described above.

The ^{13}C T_1 relaxation times were determined for the annealed 1:1 copolymer and all values for CH_2 carbons were in the range 6-8 s. These are shorter than those of crystalline regions of homopolymers, which usually range from tens to hundreds of seconds, but are comparable to those observed for poorly ordered domains in melt quenched nylon 6 and nylon 7 homopolymers,[14,16] and significantly longer than the values for the precipitated and annealed 1:1 nylon 11-co-12 sample.[20]

The X-ray results confirm the large-scale microscopic-level behavior implied by the NMR and DSC results. Figure 6 shows powder patterns for the as-precipitated and annealed samples, with the latter showing sharper and more defined peaks consistent with increased order. The characteristic pair of α-form peaks for the homopolymers (at 2θ values of 20.3 and 23.7 for nylon 6, 20.3 and 23.3 for nylon 7) gradually merge into a single peak at the 1:1 copolymer (21.5). A similar peak (in terms of 2θ value and peak shape) was observed for the 1:1 nylon 11-co-12 polymer which also exhibited characteristics of the pseudohexagonal phase.[20] Three additional points should be made. First, the patterns for the as-precipitated samples are sometimes markedly different than those of the annealed samples; see especially that of the 10% nylon 7 sample which looks essentially amorphous or perhaps pseudohexagonal before annealing but strongly α-like after. Second, all the as-precipitated patterns show a peak or shoulder at ca 2θ

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20.3 which moves to larger values for the 35:65 to 85:15 samples. Third, the top three patterns show a shoulder at 21.5 which corresponds to the γ-crystallites in these samples as confirmed by the 59 ppm shoulder in the ^{15}N spectra (Figure 4); these peaks are even stronger in the N spectra of the as-precipitated samples (not shown).

Conclusion

The synthesis of these materials clearly confirms the ready availability of high molecular weight, random copolymers of nylon 6 and nylon 7 by ring-opening lactam polymerization. DSC indicates strong enthalpic interactions and a pronounced first-order transition which appears to be a melting endotherm, but no glass transitions for the copolymers. X-ray shows a gradual merging of the characteristic α-form peaks into a single, broader peak characteristic of both amorphous and a somewhat-disordered mesomorphic state with pseudohexagonal chain packing. The solid-state NMR results indicate that the copolymers gradually decrease in α-form with increasing comonomer content until, at the 50:50 mixture, only the pseudohexagonal phase is observed. This is evident from the shift of the main ^{15}N peak from ca 84 ppm to ca 87 ppm, and by the combined changes of several of the ^{13}C peaks for the rigid-selective CPT1 experiment. The solid-state NMR results, which probe molecular level conformation and crystalline packing, thus confirm the DSC and X-ray results. Measuring both macroscopic and microscopic organization clearly shows the copolymers to be less crystalline overall but still able to accommodate the α- and γ-forms near the two compositional extremes with the thermodynamically stable pseudohexagonal form developing for the 1:1 copolymer. This pseudohexagonal phase contains more-or-less linear chains with a tightly coupled

hydrogen bond network which maintains a high degree of enthalpic interaction between adjacent chains. While this phase is not "crystalline" in the same way that the α- and γ- crystal forms are in the pure homopolymers, it represents a degree of order between those of crystallites and the amorphous region. Overall, these copolymers show that it is possible to synthetically generate a stable pseudohexagonal phase which appears to be important in poling to give piezoelectric nylon thin films. However, this phase is transient and not thermodynamically stable in homopolymer samples examined to date, and the question that needs to be addressed now is whether the stable form of the pseudohexagonal phase of the copolymers can be oriented and poled to give piezo-electric properties as well.

Acknowledgements

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16. Mathias, L. J.; Johnson, C. G. *Macromolecules,* **1991,** *24,* 6114.

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List of Figures

alpha-nylon 6
mp 225 deg C
anti-parallel chains
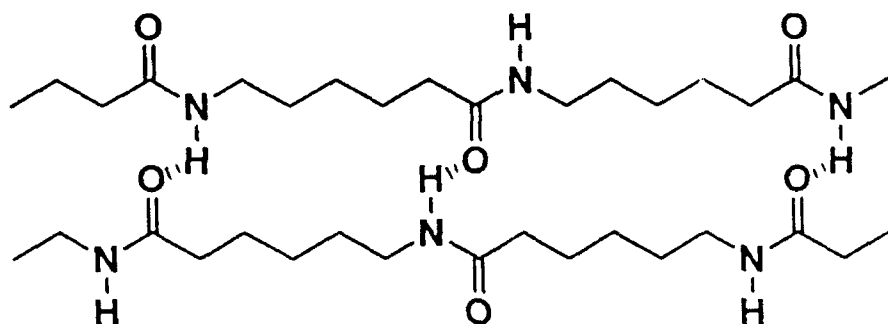
alpha-nylon 7
mp 235 deg C
anti-parallel chains

Fig 1

N7 0%

N7 15%

acetone Impurity

N7 35%

N7 50%

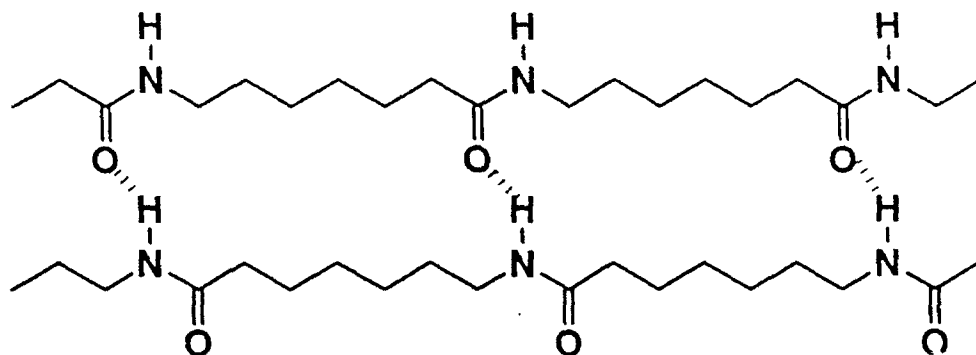N7 65%

N7 85%

N7 90%

N7 100%

45   39   33   26   20
PPM
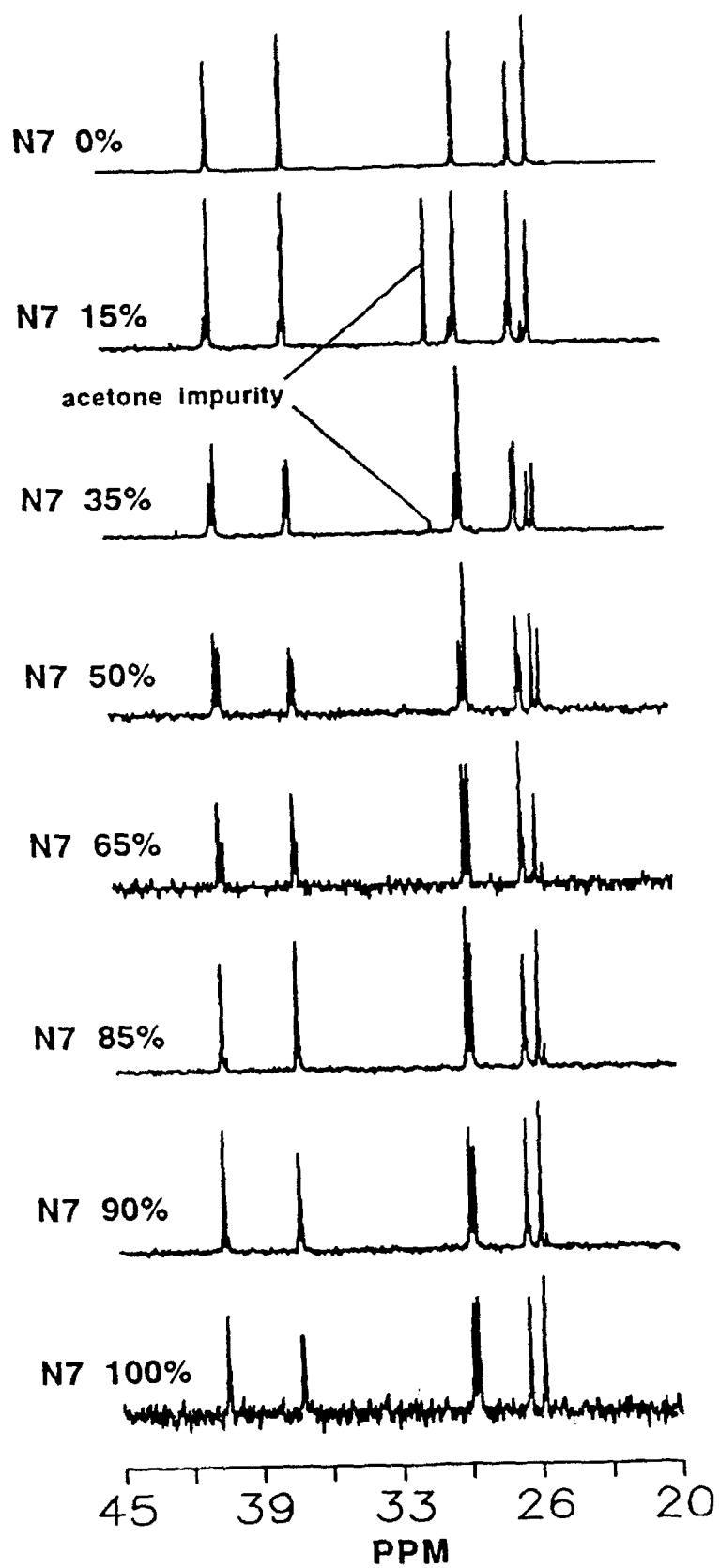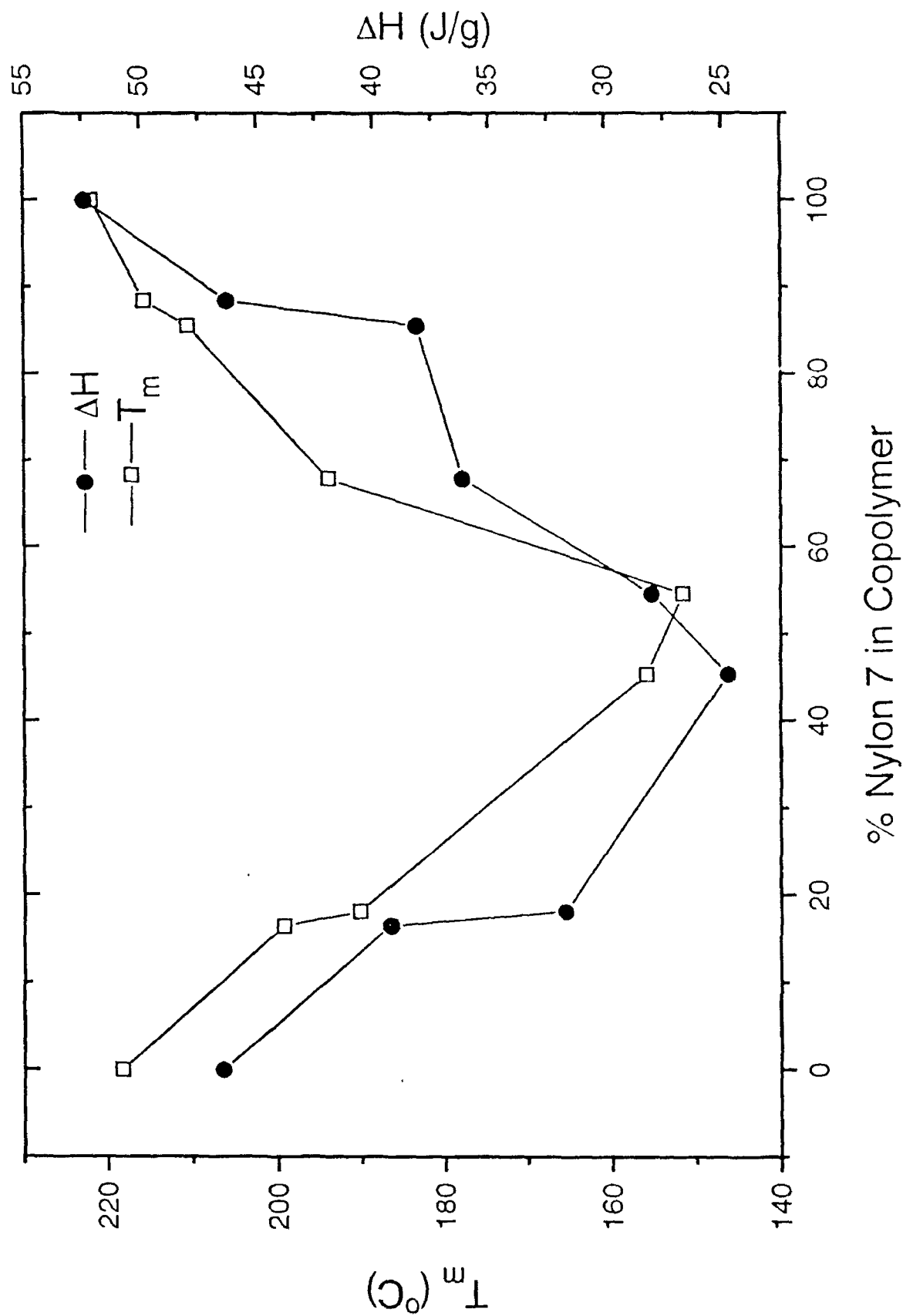
Fig 2

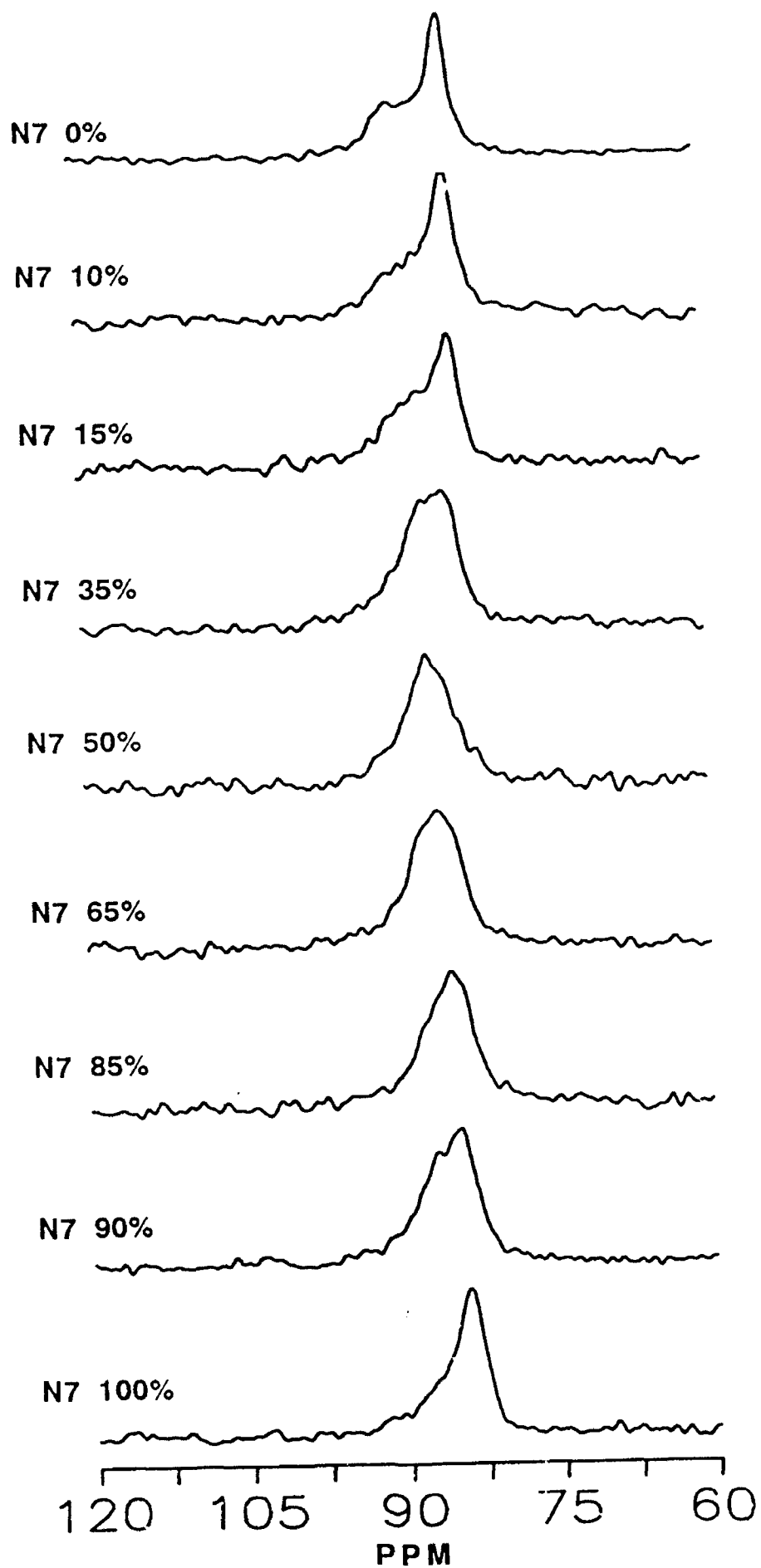Plot of T_m (left axis) and ΔH (right axis) for Nylon 6-co-7

N7 0%

N7 10%

N7 15%

N7 35%

N7 50%

N7 65%

N7 85%

N7 90%

N7 100%

120   105   90   75   60

PPM

F ig 4

N7 0%

N7 10%

N7 15%

N7 35%

N7 50%

N7 65%

N7 85%

N7 90%

N7 100%

65   50   35   20   5
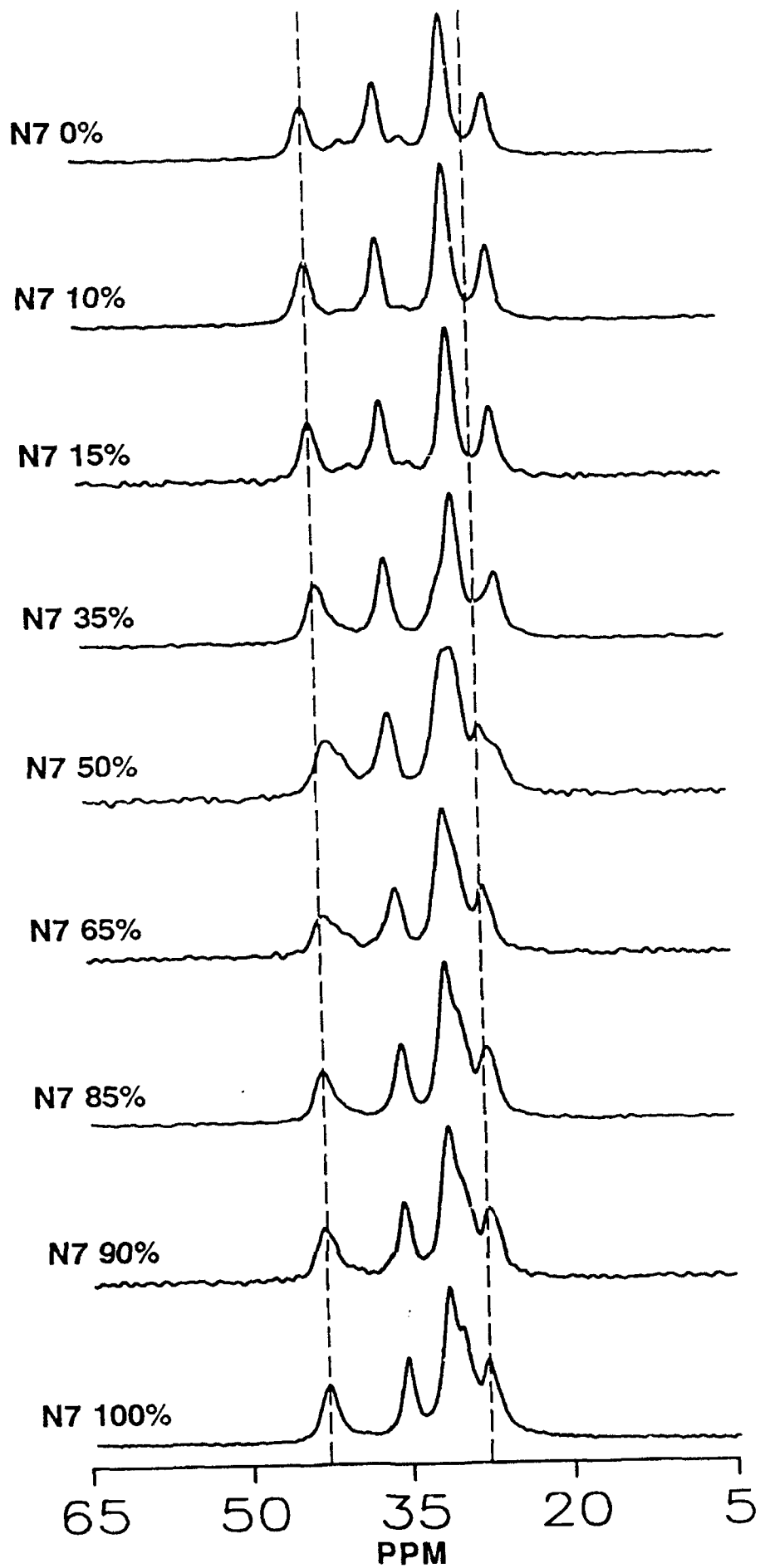PPM

Fig 5

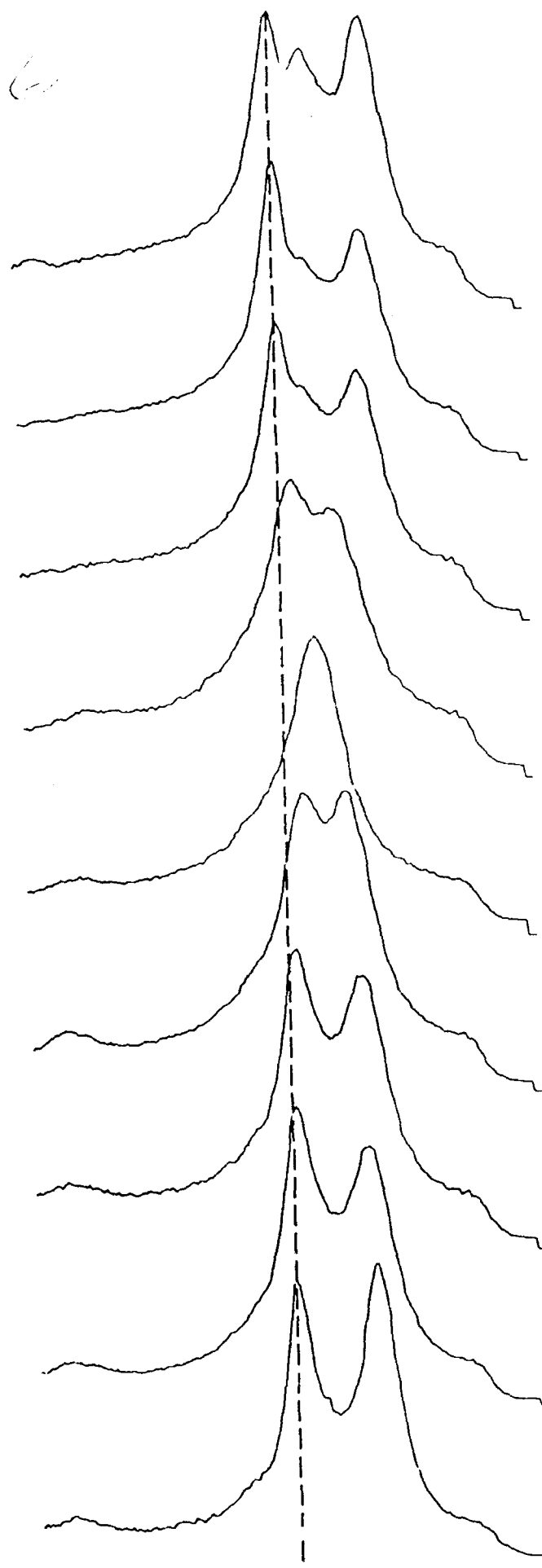N7 0%

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N7 90%

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10 12 14 16 18 20 22 24 26 28 30

10 12 14 16 18 20 22 24 26 28 30